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In this paper we investigate the causes of the chromatic alteration observed in chloroform solutions of poly (2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) after gamma ray irradiation. Structural and chemical changes were analyzed by gel permeation chromatography, fourier transform infrared spectroscopy, and proton nuclear magnetic resonance techniques and complemented by electronic structure calculations. The results indicate chlorine incorporation in the polymer structure and main chain scission after irradiation. Based on our findings we propose that the main mechanism for the blue-shifts, observed in the UV-Vis absorption spectra of MEH-PPV after irradiation, is the result of a radical attack on the polymer main chain. Gamma rays generate radicals, $\cdot\text{Cl}$ and $\cdot\text{CHCl}_2$ from chloroform radiolysis that attack preferentially the vinyl double bonds of the polymer backbone, breaking the electronic conjugation and eventually the chain. Our results indicate that oxygen does not play a major role in the effect. Electronic spectra simulations were performed based on these assumptions reproducing the UV-Vis experimental results. © 2011 American Institute of Physics. [doi:10.1063/1.3644946]

I. INTRODUCTION

Ionizing radiation is commonly used in fields such as medicine and civil construction.¹ On the other hand, inspired by the health damages associated with its absorption by the human body, there is a ceaseless interest in the research community in the development of new methods or materials that can measure dose, particularly in what concerns low doses.² In this regard, polymers and specially semiconducting polymers have been described as promising materials for the fabrication of low cost dosimeters.^{3–7}

In particular, it was reported that poly (2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) in halogenated aliphatic solvents, could be used as low dose dosimeters, <10 Gy.⁴ In Ref. 4 it is shown that MEH-PPV in solution after exposure to ionizing radiation, display a blue-shift in its main absorption peak proportional to the applied dose. On the other hand the same material in film form or in other solvents, such as toluene, are insensitive to γ -rays up to doses of approximately 100 Gy.^{4,8} The blue-shifts were explained as a decrease in the polymer conjugation length, induced by irradiation and that the solvent had a major role in the effect. However no detailed polymer degradation mechanisms were proposed.

Polymer degradation is a topic of high interest since most organic materials are subject to decay under excitation, like for example under UV illumination.^{9,10} In the case of semiconducting polymers this topic is of particular relevance, since devices based on these materials have their performance strongly affected by photo-oxidation.^{9–13} It is well established in the literature that in these systems oxygen and water plays a crucial role in the polymer degradation.^{10,11} In the case of PPV derivatives, the main reaction mechanism is believed to be the addition of singlet oxygen in the vinyl group¹⁴ or the abstraction of labile hydrogen atom in the α position of the ether. This initiates the chain oxidation by fixation of oxygen, involving peroxy and alkyl radicals.¹¹ Another possibility is

the formation of radical cation of the PPV derivative in the presence of oxygen.¹¹ In this case, ($\text{O}_2^{\bullet-}$) cannot be considered as responsible for the propagation of the oxidation. The main role of oxygen is to favor the formation of the $\text{PPV}^{\bullet+}$ radical cations. The radical cations are likely to initiate a chain oxidation process by fixation of fundamental O_2 or by reacting with superoxide anion ($\text{O}_2^{\bullet-}$) as described by Scoponi *et al.*¹⁵ In both cases, the abstraction of labile hydrogen in the ether position occurs. There is a vast literature in these subject, however not when ionizing radiation is used.^{10–13,16,17}

The effects of gamma radiation observed in polymers are diverse and depend on several factors, such as temperature, chemical environment, chemical structure, as well as the polymer physical state.^{18–20} For example, the irradiation of polyethylene under inert atmosphere results in cross-linking.²¹ On the other hand, if the atmosphere during irradiation contains reactive species, such as oxygen, scission reactions are observed, due to the action of peroxide.^{18,21–23} In this case photons are absorbed by the polymer creating radicals that react with oxygen or peroxide that induce scission.²⁰ As mentioned in the case of MEH-PPV in solution it was proposed that the solvent had a major role in the polymer degradation. It is well known that halide solvents under ionizing irradiation do form radicals,²⁴ however the effect of these radicals on conjugated polymers have not been studied systematically. In this work, we present a detailed investigation on the effects of ionizing radiation on the chemical structure of MEH-PPV in halogenated solvents.

II. MATERIALS AND METHODS

A. Experimental

Poly (2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) with mean molecular weight from 70000 to 100000 was purchased from ALDRICH (Milwaukee, USA).

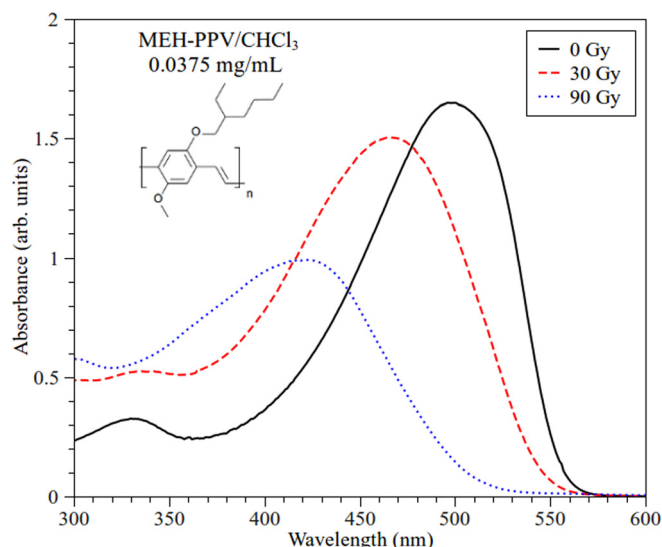


FIG. 1. (Color online) UV-Vis absorption spectra of 0.0375 mg/mL MEHPPV solutions in chloroform, before (solid line) and after irradiation with 30 Gy (dashed line) and 90 Gy (dotted line).

The main polymer structure is shown in Fig. 1. Chloroform, CHCl_3 , was purchased from ACROS (New Jersey, USA). Polymer, reagents, and solvents were used as received.

MEH-PPV solutions were prepared at room temperature under weak illumination conditions to avoid photo-degradation.²⁵ Solutions were kept in 4 mL glass recipients (Wheaton 13-425) and irradiated with a ^{60}Co gamma ray source (1.25 MeV, SIEMENS GAMATRON S-80) with appropriate acrylic build-ups.

The concentrations used ranged from 0.0125 mg/mL to 0.225 mg/mL. All solutions have been prepared at room temperature under low illumination conditions to avoid undesirable photoreactions and stored in a refrigerator ($T = 283$ K). For each concentration five samples have been prepared, one was kept as a reference, while the other four irradiated in pairs in order to test reproducibility. The samples have been irradiated at room temperature in a cobalt therapy unit (CGR - Model Alcyon II) with appropriate acrylic build-ups (thickness of 0.5 cm), at a rate of 0.5 Gy/min. The doses used were 30 and 90 Gy.

The UV/Vis absorption spectra of MEH-PPV solutions were measured using a SHIMADZU UVMINI 1240 spectrometer. Infrared spectra were obtained from MEH-PPV films that were deposited directly in the ZSM-5 cells. For the FTIR measurements a Bruker Vertex 70 Fourier Transform spectrometer was used. Gel permeation chromatography (GPC) measurements were performed on an Agilent 1100 series system with PSS-SDV (5 μm , 100 and 1000 \AA) columns, THF as eluent (at 35 $^\circ\text{C}$, flow rate 1 mL/min) and calibration using a PSS-ReadyCal Kit of poly(styrene) (PS) (MP = 480 - 2500000 Da) standards. For sample preparation, 50 $\mu\text{g}/\text{mL}$ solutions of MEH-PPV in chloroform were irradiated with 20 Gy of gamma radiation and subsequently the solvent was completely evaporated. 2 mg of MEH-PPV (irradiated or non-irradiated, from the same batch) was dissolved in 1 mL THF and 100 μL of this solution was injected. Data acquisi-

tion and analysis were carried on WinGPC software from Polymer Standards Service GmbH (PSS).

^1H and ^{13}C NMR were obtained in using a 400 and 500 MHz spectrometer from Bruker DRX 400. For these measurements, the MEH-PPV solutions were evaporated under reduced pressure and then dissolved in deuterated chloroform (CDCl_3) (99.8% chloroform- d - Aldrich) at a concentration of 10 mg/mL. The chemical shifts were referenced to tetramethylsilane (TMS) and chloroform- d_1 in the case of ^1H -NMR and ^{13}C -NMR, respectively. Additionally, gradient-selected H, C shift correlation experiments (gs-H, C HSQC) were carried out.

B. Electronic structure calculations

The structure optimization was performed with a restricted Hartree-Fock (RHF) approach using the PM3 semi-empirical method implemented in the MOPAC 2007 software package.²⁶ Initially the steric interaction between the lateral branches of adjacent units were investigated. For that purpose the conformation of these branches were optimized by molecular dynamics calculations of tetramers. Larger structures were made using the lowest energy conformation obtained from the tetramers study. The solvent was simulated by the COSMO continuum method.²⁷

The reactivity study was performed using Fukui indices analysis. The Fukui function, $f(\vec{r})$, describes how the electron density varies in response to electrons removal or addition in a system, with the geometry fixed. Within an adiabatic approximation, one can assume that a variation in the electrons number is directly related to a change in the frontier orbitals electron density of the system (HOMO and LUMO). Thus, it carries information about how the frontier orbitals are modified by varying the electrons number, and has been employed in order to understand and predict the reactivity variation in different sites of a molecule.²⁸⁻³⁰

Practical ways to calculate these indices, proposed by Yang and Mortier,³¹ are known as the condensed-to-atoms Fukui indices (CAFI). Given a system M with N electrons whose reactivity we want to study, when receiving an electron the system becomes M^{-1} , with $(N+1)$ electrons and losing an electron we have M^{+1} , with $(N-1)$ electrons. The CAFI is then expressed by

$$\begin{aligned} f_k^+ &= q_k(N+1) - q_k(N) \quad \text{nucleophilic attack} \\ f_k^- &= q_k(N) - q_k(N-1) \quad \text{electrophilic attack} \\ f_k^0 &= \frac{1}{2}[q_k(N+1) - q_k(N-1)] \quad \text{radical attack} \end{aligned}$$

where $q_k(N+1)$, $q_k(N)$ and $q_k(N-1)$ represent the electron population on the k th atom in the species M^{-1} , M , and M^{+1} , respectively. The functions f^+ , f^- and f^0 are used for reactions analysis involving nucleophilic, electrophilic, and free radical attacks, respectively. The higher the values of these functions the higher the reactivity of the site.

It is well known that in general polymers do not present a completely planar structure; the main chain can twist introducing random physical defects, which prevents the π system to extend throughout the structure.³² For MEH-PPV,

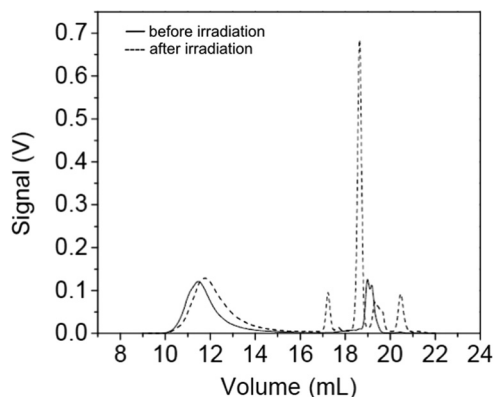


FIG. 2. GPC eluogram of non-irradiated (solid line) and irradiated (dashed line) MEH-PPV solutions.

especially, evidence shows that the polymer chains can be considered as a collection of approximately planar segments with different conjugation lengths, with an average of 10 repeating units.³³ Thus the CAFI study was performed using a MEH-PPV decamer.

The indices were calculated using density functional theory (DFT) with Becke's LYP (B3LYP/VWN5) exchange-correlation functional; for all atoms, 6-31 G basis set was adopted. To calculate the electronic population of the neutral species, we used the restricted Kohn-Sham (RKS) approach. For charged species, with the insertion and removal of an electron, we used the restricted open-shell Kohn-Sham (ROKS) approach, to avoid spin contamination.^{34,35}

The electronic populations were obtained by charge calculation with electrostatic potential (ESP) fitting³⁵ and Mulliken population analysis,³⁰ the solvent was again simulated by the COSMO continuum method. Calculations were performed with the Firefly/PCGAMESS computer package.³⁶

The theoretical optical absorption spectra for all structures were calculated with the Orca software package.³⁷ We used a RHF approach with the ZINDO/S semiempirical method in conjunction with the CIS method. Such methods have proved suitable for vertical excitation energies of medium and large molecules, including transition-metals compounds.³⁵

TABLE I. IR band positions of non-irradiated MEH-PPV.

Wavenumber (cm ⁻¹)	Assignment
3065	CH – stretching vinyl
2956	CH ₃ asymmetric stretching
2919	CH – stretching
2850	CH ₂ stretching
1506	Semicircular phenyl stretch (C-C aromatic)
1492	Semicircular phenyl stretch (C-C aromatic)
1464	Anti-symmetric alkyl CH ₂ stretch
1412	Semicircular phenyl stretch
1379	Symmetric alkyl CH ₂ deformation
1204	Phenyl oxygen stretch
1078	Alkyl oxygen stretch
1039	Alkyl oxygen stretch
970	<i>trans</i> -double bond CH-wag (vinyl group)
860	1,2,5,6 Tetra-substituted benzene ring bend

III. RESULTS

Figure 1 shows the absorption spectra of samples with 0.0375 mg/mL, before and after irradiation with doses of 30 and 90 Gy. The main peak in the non-irradiated solutions, at 500 nm, is attributed to the transition between the MEH-PPV frontier orbitals of π - π^* .³⁵ A second peak at 330 nm is also seen, characteristic of polyphenylene derivatives, and attributed to forbidden transitions allowed by symmetry breaking.³⁸ After irradiation, a blue-shift in the main peak position is observed as expected.⁴

As mentioned in the Introduction, the shift in the main peak is assigned to a decrease in conjugation length. One source of the decrease in conjugation length is chain scission, which can be measured using gel permeation chromatography (GPC), see Fig. 2.

In Fig. 2, the eluogram of MEH-PPV before and after irradiation is presented. The eluogram displays a broad peak at around 11 mL which shifts to higher volumes after irradiation, this corresponds to a decrease in molecular weight, from $M_n = 61000$ to about $M_n = 43000$ g/mol. The peak at low molecular weights (higher volumes) comes from

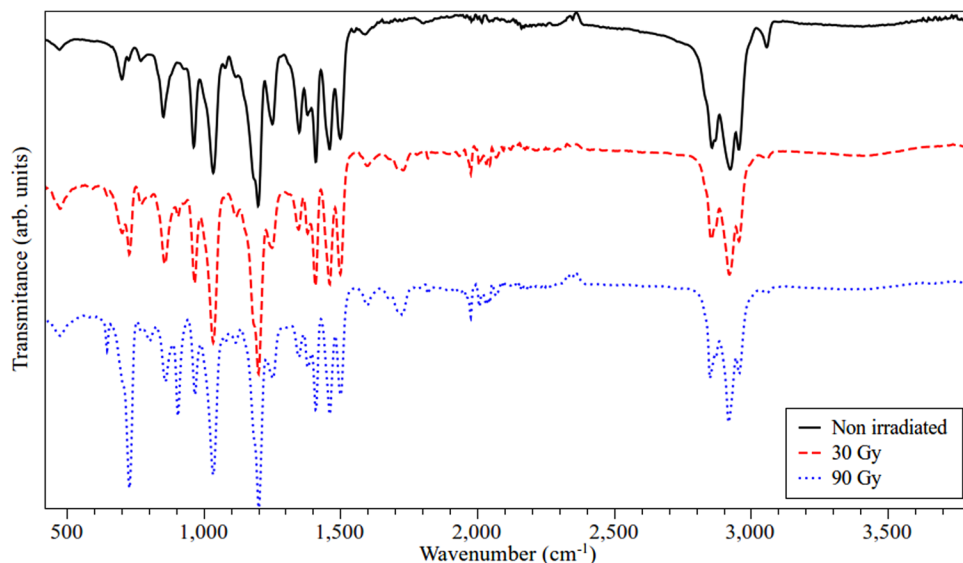


FIG. 3. (Color online) FTIR spectra of MEH-PPV chloroform solution of non-irradiated (solid line), irradiated solution with 30 Gy (dashed line) and irradiated with 90 Gy (dotted line).

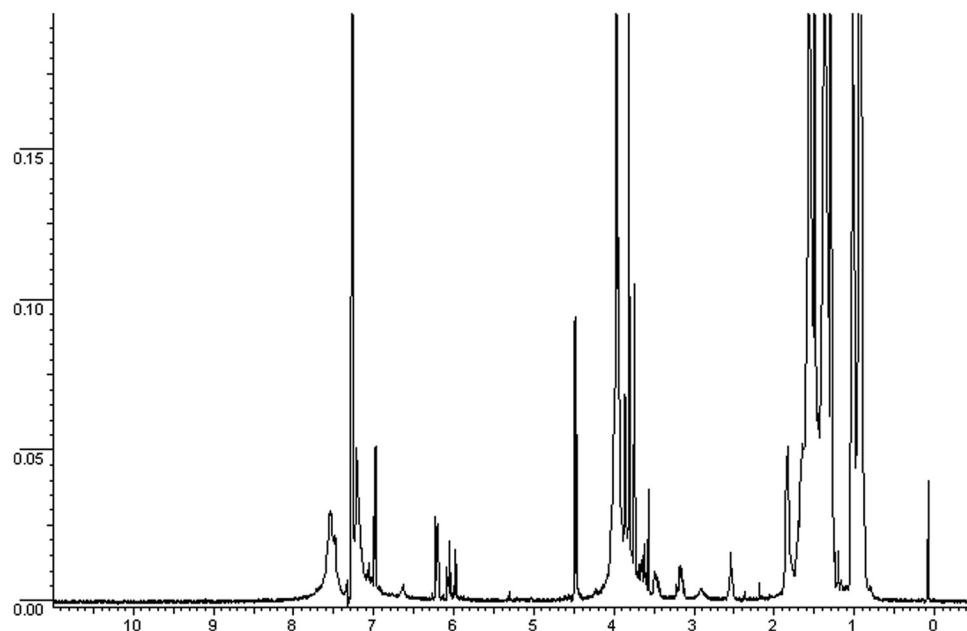


FIG. 4. ^1H NMR spectra of MEH-PPV in CDCl_3 solution before irradiation.

impurities, probably smaller MEH-PPV segments left over from the synthesis. Remember that no purification step was employed, and the MEH-PPV was used as bought. We do not believe that such impurities have a significant role in the modifications observed after gamma irradiation, as will be discussed later. The shift of the main GPC peak to higher volumes is a clear indication that MEH-PPV suffered scission of its backbone chain upon irradiation.

Figure 3 shows the FTIR spectra of MEH-PPV solutions before and after irradiation (0.225 mg/mL, 30 and 90 Gy). The main bands and their assignments for the non irradiated polymer are listed in Table I. New bands at 648, 729, and 906 cm^{-1} can be observed after irradiation, which are clear indications that halogen atoms are added to the polymer chain. The spectra are normalized to the Ph-OR stretching

band at 1204 cm^{-1} to remove the influence of small differences in the baseline.³⁹ This band was chosen since it does not change after irradiation.^{12,13} Notice that weak bands can be seen at $1680\text{--}1720\text{ cm}^{-1}$. We believe that these bands are due to $\text{C}=\text{O}$ and appeared as a result of MEH-PPV manipulation and not as a result of gamma irradiation, as will be discussed later on. The oxidation, as a result of sample manipulation, is commonly reported in the literature.⁴⁰

Figure 4 shows the ^1H NMR spectrum of non-irradiated MEH-PPV in chloroform. These spectra match what is reported in the literature with peaks found in 7.52 (2 H, d, CH), 7.19 (2 H, s, CH), 3.94-3.97 (5 H, m, OCH_2 and OCH_3), 1.15-1.90 (9 H, m, CH_2 and CH), and 0.82-1.05 ppm (6 H, m, CH_3).¹⁴ Signals related to structural defects from the polymer synthesis are also shown at low proportions

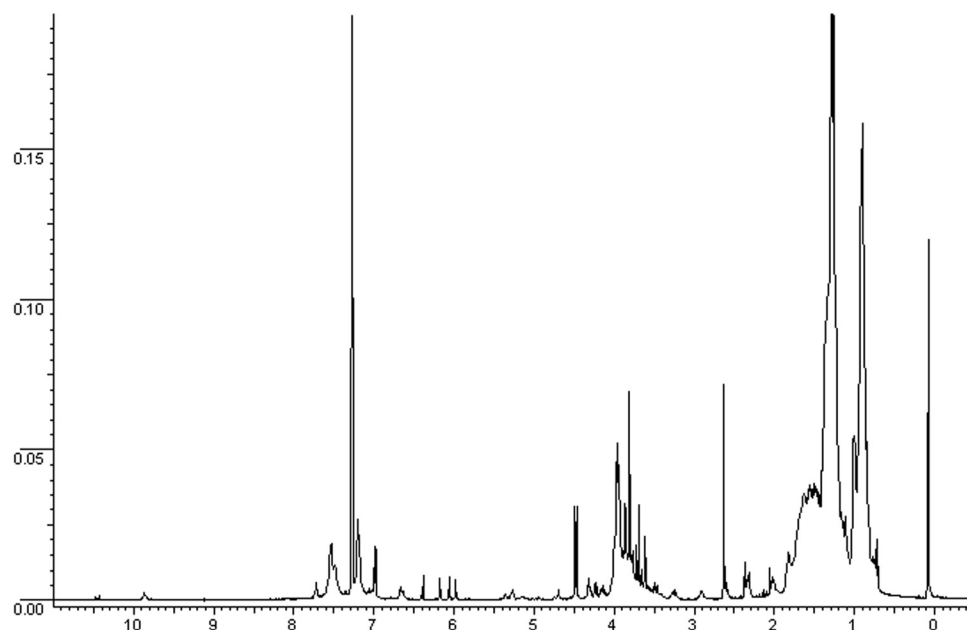


FIG. 5. ^1H NMR spectra of MEH-PPV in CDCl_3 solution after irradiation with 30 Gy.

(2.4 – 3.2, 4.4 – 4.5 e 5.9 – 6.3 ppm) and may be associated with non-conjugated portions of the polymer chain.^{40,41}

After irradiation, as presented in Fig. 5, new signals are observed in different regions of the spectrum with low intensity (2.5–3.5, 4.5–5.5, and 5.5–6.5 ppm). The initial structural defects are still present with small alterations. The spectral changes give us a strong indication of structural changes in the polymer chain. For instance, the signals at 4.70, 5.09, and 5.53 ppm are typical of protons adjacent to chlorine atoms, as will be discussed in more detail in the next section. The signals at 9.85 and 10.45 ppm are typical of MEH-PPV oxidation after manipulation of irradiated samples.

The analysis of the ¹H NMR spectrum suggests that most of the impurities observed in Fig. 2 are due to smaller fragments of the polymer. The signs of these structures can not be resolved in the ¹H NMR spectrum since they present the same shifts of larger polymer chains.

¹³C NMR spectra signals obtained were very weak, due to sample size, even with acquisition times of 13 h. The gs-H, C-HSQC spectrum was also performed, but for the same reasons noted for the ¹³C NMR, it has not provided a deeper insight into the study (see Supplementary Information for details⁴²).

IV. DISCUSSION

As mentioned, the effects of gamma radiation on polymers are diverse and depend mainly on the polymer structure and the chemical environment in which the irradiation occurs. The action of ionizing radiation is known to modify the structure of conjugated polymers. It may induce cross-linking or scission of backbone chains, changing the number and the nature of the double bonds. The cross-linking reactions lead to the formation of inter- and intramolecular bonds, which increase the molecular weight. In contrast, scission reactions lead to polymer chain cleavage, decreasing the molecular weight and the formation of several sub-products.⁴³

In our case we have not observed any direct evidence of cross-linking reactions, however in some cases for very high doses, we could observed that the polymer solution became a viscous solution after mild heat treatments. As the solvent evaporated instead of having simply the polymer powder, a gel was formed. As can be seen in Fig. 2, the decrease in molecular weight, from Mn = 61000 to about Mn = 43000g/mol, clearly shows that the polymer backbones did break after irradiation. The scission can be associated with the attack of reactive chemical species or the direct interaction of the polymer chain with the ionizing radiation.

We will consider first the latter hypothesis. According to Chambon *et al.*¹¹ the irradiation can initiate polymer degradation by abstraction of the labile hydrogen atom in the α position of the ether function, with subsequent radical reactions. Another possibility is the homolytical scission of the –O–CH₂ bond (induced by irradiation), which promotes the formation of two radicals that immediately recombine or add on double bonds causing the conjugation reduction.^{12,13} This hypothesis is not compatible with our IR spectra (see Fig. 3). The IR spectra of our samples do not show a decrease in the bands assigned to the ether at 1205, 1078, and 1035 cm^{–1}, as

discussed by Chambon *et al.*^{12,13} Moreover, as already mentioned in the Introduction, MEH-PPV films are insensitive to γ -irradiation. More importantly, MEH-PPV dissolved in toluene is also insensitive to γ -irradiation.⁸ Thus in the following discussion we shall not consider the direct absorption of γ -rays by the polymer chain as the main mechanism of degradation.

We shall now consider the hypothesis of the formation of reactive species as a consequence of irradiation that attacks the polymer. As already mentioned, the most well-known polymer photo-degradation mechanism in conjugated polymers involves chain oxidation. The presence of oxygen and water during irradiation favors scission reactions¹⁸ due to the oxidative activity of peroxy and alkoxy radicals in PPV derivatives.²⁰ These reactions produce aromatic ketone, aromatic aldehyde, alcohol, and carboxylic acid, as main by-products and frequently are responsible for the conjugation reduction in these systems, promoting a blue-shift in the UV/Vis absorbance. However, as already mentioned, the effect is dependent on the solvent used, for example, in toluene solutions the photo-degradation is absent. Since the amount of oxygen and water should be approximately the same in chloroform as well as toluene, we do not believe that oxygen or water is the main reactive species in our experiments. In fact, the solubility of oxygen in these solvents is very similar at room temperature.^{44,45} Notice also that in our study, we avoided as much as possible exposing our samples to oxygen/air and light, in order to avoid the photo oxidation reactions, and we employed different solvent batches. However, water and oxygen is certainly present since our samples were prepared and processed in air. For example, for NMR and FTIR measurements, the solvent was evaporated in air, the powder obtained was re-dissolved in deuterated chloroform in the case of NMR, or the manipulation samples for FTIR, as describe in the experimental part. So, as can be seen in Fig. 3 small bands in the region 1680–1720 cm^{–1} are observed after irradiation which is assigned to carbonyl groups.^{9,10,40} Notice that MEH-PPV is extremely susceptible to oxidation when exposed to air.^{10,40} This hypothesis is reinforced by the fact the bands related to oxidation are similar independent of the dose used 30 and 90 Gy. Therefore we can conclude that oxidation is not the main process responsible for the blue-shift in the absorption bands of MEH-PPV after irradiation.

Considering the possibility of reactive species formation from the solvent, it is known that chloroform is unstable under ionizing radiation,²⁴ forming radicals as described by the following reaction:



Thus let us consider the hypothesis of the attack of these radicals to the polymer chain as the main degradation mechanism. Considering the MEH-PPV polymer chain (see Scheme 1), there are four regions where the reaction, substitution or addition, can occur: the phenylene ring, the vinyl, the methoxy, and the alkoxy groups. Labile hydrogen abstraction is also possible, as already mentioned and in agreement with the literature.⁴⁶

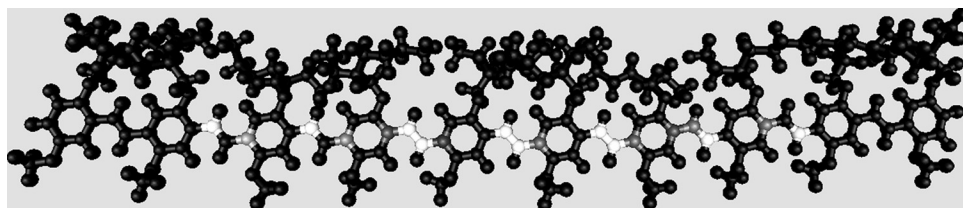


FIG. 6. Fukui indices (f^0) calculated using the ESP charges on the atoms of the MEH-PPV decamer.

Thus in order to evaluate the mechanisms involved in the spectra alterations and identify the most susceptible regions to radical attack in the polymer backbone, electronic structure calculations were performed. Figure 6 illustrates the Fukui indices associated to radical attack on the MEH-PPV decamer using the ESP charges to evaluate the electronic populations. Similar results are obtained using Mulliken population analysis. The dark and light regions delimit the minimum and maximum indices, respectively.

Note that the central vinyl groups are the most susceptible sites to radical attack. In this regard, different mechanisms can be considered: *i*) double bond saturation by radical incorporation or/and *ii*) scission of the polymer chain induced by addition of radicals in the vinyl double bond. In both cases, a reduction in the polymer conjugation length and a blue-shift in absorption spectra are expected, in agreement with the experimental results.

From Eq. (1), the main by-products formed from chloroform irradiation are $\bullet\text{CHCl}_2$ and $\text{Cl}\bullet$. However, due to steric factors it is reasonable to assume that chlorine radicals are more likely to react. In fact, it is known that chlorine radicals present higher reaction rates constants than $\bullet\text{CHCl}_2$ in liquid phase.⁴⁷ In this sense, the radical attack was simulated by chlorine incorporation on different vinyl groups in the polymer chain. However similar results should be obtained if one considers $\bullet\text{CHCl}_2$.

Table II shows the main peak position (λ_{max}) and its shifts ($\Delta\lambda$), relative to the unmodified structure, for attacked decamers in different regions of the polymer backbone (unmodified polymer; 1: with chlorine incorporated in the first vinyl group, between the first and second repeating units; 2: radical incorporation in the second vinyl group, between second and third repeating units; etc.; for details see the Supplementary Information).⁴² As expected, the most noticeable changes are observed when the central regions of the polymer chain (region 5) are attacked. Remember that

TABLE II. Main peak position of optimized structures after chlorine incorporation in different regions of the polymer backbone (for details, see Supplementary Information⁴²).

Attacked region	λ_{max} (nm)	$\Delta\lambda_{\text{max}}$ (nm)
1	438.773	4.660
2	435.504	7.929
3	432.924	10.509
4	426.606	16.827
5	422.902	20.531
Non-attacked	443.433	...

the central regions are the most susceptible sites as obtained from the Fukui indices analysis.

It is well known that the polymer absorption spectrum is composed of a non-homogeneous superposition of the absorption of planar substructures (chromophores) present in the main chain.³² Our calculations reproduce this effect (see Supplementary Information⁴²). For example, considering the radical incorporation in region 2 (between the second and third units), the main peak shifts to shorter wavelengths (435 nm) and a new weak peak is formed at 325 nm, which is consistent with octamer and dimer substructures resulting after the radical attack. The spectrum is dominated by the larger substructures (with more electrons), in this case the octamer units. Similar considerations can be made for incorporations in the other regions.

MEH-PPV absorption spectra were simulated following this idea. For that purpose it was considered a polymer main chain with 330 units (82000 g/mol) constituted by chromophores with different conjugation length, randomly distributed between 1 and 20 units. As a first approximation, the π system overlap between adjacent chromophores were neglected, thus, the polymer spectra were calculated from the chromophores spectra sum weighted by the number of units present in each substructure. Averages of 10000 distinct polymeric chains, randomly generated, were considered. The main peak position of each substructure were obtained using a linear regression equation using as input data the result of electronic structure calculations of substructures with 4, 5, 6, 8, and 10 units (see Supplementary Information⁴²). The chromophores spectrum was simulated using Lorentzian curves.

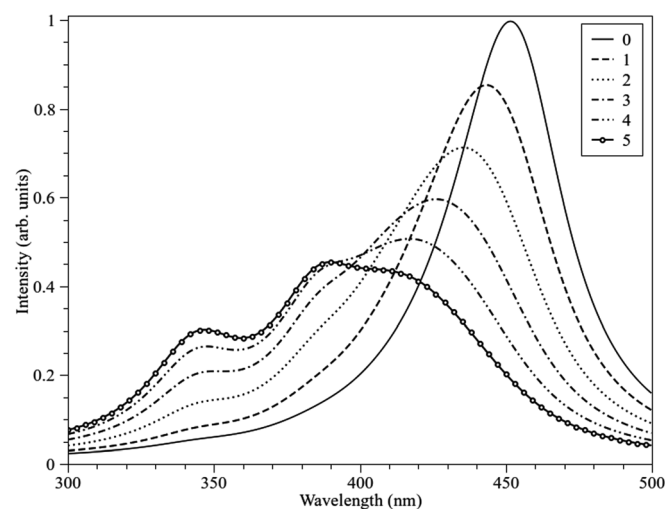
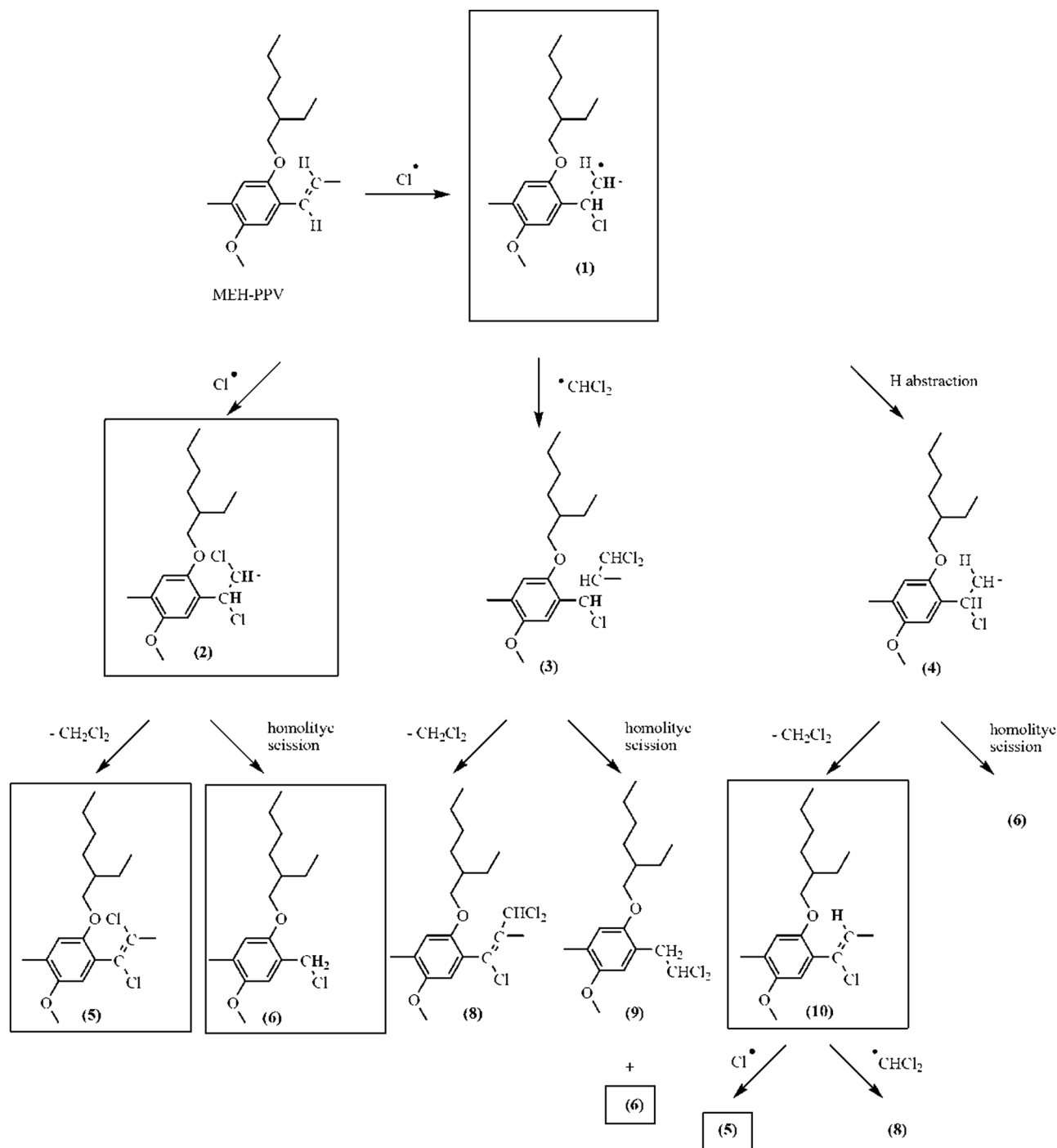


FIG. 7. Theoretical optical absorption spectra for structures attacked in the regions 1, 2, 3, 4, and 5 of the polymer backbone. 0 represents the unmodified decamer spectrum.



SCHEME 1. Proposed MEH-PPV degradation by alkyl halide radicals that induce blue-shifts in the absorption spectra. The radicals were formed by γ induced dissociation of CHCl_3 . The products highlighted are related to H-NMR signals observed in Fig. 5.

The radical attacks were simulated by chlorine incorporation in the central vinyl group of each planar substructure. Attacks on the adjacent vinyl groups, were considered less likely to occur, as indicated by Fukui indices. Figure 7 illustrates the resulting effect. The number 0 represents structures that have not suffered attack. Data regarding the amount of substructure present in each spectrum are shown in the Supplementary Information.⁴²

It is found, as expected, that larger structures are more susceptible to radical attack due to the greater number of regions susceptible to attack, or, in other words, the greater number of vinyl groups. The irradiation promotes an increase

in the population of smaller structures due to radical incorporation in the polymer substructures. The polymer spectrum is then dominated by these smaller substructures, resulting in a blue-shift in the spectrum, in good agreement with what is seen in Fig. 1.

Support to the hypothesis of chlorine incorporation in the main chain is found in the analysis of FTIR. The band positions of the FTIR, Fig. 3, did not change significantly after irradiation, indicating little or no change in the vibrational environment of these bands. After irradiation new absorption bands at 648 cm^{-1} , 729 cm^{-1} , and 906 cm^{-1} are observed, assigned to C-Cl, $-\text{CCl}_2$, $-\text{CHCl}$ or $-\text{CH}_2\text{Cl}_2$ stretching. The

clearest change is the band at 729 cm^{-1} related to $-\text{CCl}$ or $-\text{CCl}_2$ stretching.⁴⁸ Another indication of the addition in vinyl double bond after irradiation, is the decrease of the band in 3065 cm^{-1} , which is assigned to C-H stretching from the vinyl group. Notice that the process of chlorine addition is clearly dependent on the irradiation dose.

Similar effects were observed in ^1H NMR. As mentioned before, commercial polymers can have structural defects due to impurities or residues of the synthesis. The signals in 2.7–2.8, 6.6, and 6.7–6.8 ppm are attributed to tolane bis-benzyl defects and cis-configured vinylene moieties.⁴¹ Other signals especially in the range of 2.5–3.5 and 5.5–6.5 ppm are assigned to defects. These fragments, initially present as defects, changed after irradiation, which is a clear indication that radical have been created after irradiation. These structures are more unstable, and thus susceptible to radical addition. However, there is no evidence that these defects participate in the chromatic alteration mechanism, since these fragments have shorter conjugation lengths, it does not affect the absorption spectrum of the polymer significantly. In addition the same effect has been observed in different polymer batches, with different defects amount.

The most important observation, in what concerns chlorine addition, are the signals at 4.7 and 7.2 ppm associated with chloromethylene protons of the $-\text{CH}_2\text{Cl}$ (one singlet as a result of unsymmetrical substitution) and nearby aromatic protons, respectively. The signal in 5.46 ppm is also attributed to the addition of two chlorine atoms in the polymer chain, following what is reported in the literature and ^1H NMR simulations using Chem Draw Ultra.⁴⁹ The presence of chlorine addition/substitution could be confirmed by spin-spin coupling (J_{HH}) analysis. However, given the resolution obtained in the ^1H NMR spectrum was not possible to obtain the J_{HH} value.

In summary, our results indicate that the origin of the effects observed is the result of chlorine radical attack to the vinyl groups of MEH-PPV. Our theoretical simulations indicate that the phenylene ring is less reactive than the vinyl group. Thus we shall not consider the participation of the ring in the effect. The same theoretical simulation shows that substitutions on the methoxy or alkoxy group should not influence the optical properties of the polymer (not shown). From what has been discussed so far, the following reaction mechanism is proposed. Notice however that at this point one cannot give a detailed description of the reaction.

The first step is the γ induced dissociation of the solvent, Eq. (1). Following this dissociation, the two radicals formed attack the polymer chain. From reactivity and steric considerations it is assumed that the addition and substitution reactions are mainly due to $\bullet\text{Cl}$ and not $\bullet\text{CHCl}_2$ (see Ref. 50) after H abstractions from the polymer chain. An indication in favor of this hypothesis is the formation of CH_2Cl_2 , as seen from H-NMR data published elsewhere.⁸ As already mentioned, we are only considering here reactions involving the backbone chain. $\bullet\text{Cl}$ is added to the vinyl group of MEH-PPV creating a new radical that sits close to Cl, Scheme 1. This secondary radical is highly reactive, so in the following the species available for reaction, $\bullet\text{Cl}$, $\bullet\text{CHCl}_2$ are added or substituted in a series of concatenated reactions, some of which are represented

in the same scheme. This series of reactions can lead to chain scission, products 6 and 9 in the scheme.

Our results are in good agreement with previous reports that shows that the introduction of electron-withdrawing substituent, and in particular halogen atoms, in the conjugated backbone, has profound effect in the bandgap, emission properties, and electron injection properties of PPV polymers.⁵¹ For example, PPVs with fluorine atoms in the back bone⁵² show a blue-shift in the absorption peak, with respect to pure PPV.

V. CONCLUSIONS

We have investigated the origin of blue-shifts in the MEH-PPV absorption band after γ irradiation. Our results indicate that the main mechanism for the blue-shifts is indirect. Chloroform absorbs γ rays that produce its dissociation into chlorine radicals. These radicals attack the polymer chain preferentially in central vinyl bonds; according to reactivity calculations performed using Fukui indices. The radical $\bullet\text{Cl}$ is added to C double bonds or substitute H leading to a decrease in conjugation length and eventually to chain scission. Our results indicate that oxygen does not play a major role in the effect. Theoretical electronic spectra simulations were performed based on these assumptions reproducing the UV-Vis experimental results.

Our findings on the polymer-solvent radiation interaction shall help the development of more sensitive polymer-based dosimeters.

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